Supporting Information

for

Primary-tertiary diamine-catalyzed Michael addition of ketones to isatylidenemalononitrile derivatives

Akshay Kumar and Swapandeep Singh Chimni*

Address: Department of Chemistry, U.G.C. Centre of Advance Studies in Chemistry, Guru Nanak Dev University, Amritsar, 143005, India; Fax: (+)91-183-2258820

Email: Swapandeep Singh Chimni - sschimni@yahoo.com

*Corresponding author

Experimental procedures, copies of ^{1}H and ^{13}C NMR spectra of Michael adducts and HPLC chromatogram of products **4**

Table of Contents

General Remarks

All reagents were commercially available and were used without purification. Isatylidenemalononitrile derivatives **3** were prepared according to the reported procedure [1]. The primary-tertiary diamines were prepared according to our previously reported method [2]. NMR spectra were obtained at 300 MHz for ^{1}H NMR and at 75 MHz for ^{13}C NMR in $CDCl_3$ with Me_4Si as internal standard. The chemical shifts are reported on δ scale relative to TMS and coupling constants *J* are expressed in Hz. Spectral patterns are designated as s = singlet; d = doublet; dd = doublet of doublet; t = triplet; br = broad; m = multiplet. Optical rotations were determined on a digital polarimeter. Column chromatography was carried out on a with silica gel (60–120 mesh) using increasing concentration of ethyl acetate in hexane as eluent. HPLC analysis was performed using Daicel Chiralpak AD-H, AS-H, OD-H and IB columns.

General procedure for enantioselective Michael addition of ketone 2 to isatylidenemalononitriles 3.

To a stirred mixture of catalyst **1a** (2.33 mg, 0.0125 mmol), ketone **2** (0.11 mL, 1.5 mmol) in 1,2-dichloroethane (1.5 mL), the additive D-CSA (2.91 mg, 0.0125 mmol) was added at 25 °C and the mixture was allowed to stir for 2 min followed by the addition of the corresponding isatylidenemalononitrile derivative (0.125 mmol). The resulting mixture was stirred for 24–168 h and the progress of the reaction was monitored at regular intervals by TLC. After completion of the reaction, saturated solution of NH_4Cl (3 mL) was added and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was separated, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to obtain the crude Michael product. Subsequent purification by column chromatography gave the corresponding pure Michael adducts. The enantiomeric excess of the products was determined using Diacel Chiralpak AS-H, OD-H, AD-H and IB columns. Racemic standards were prepared using (±)-3-methyl-1-morpholinobutan-2-amine as catalyst synthesized from (±)-valine.

General Procedure for three component enantioselective Michael reaction

To a stirred mixture of catalyst **1a** (2.33 mg, 0.0125 mmol), acetone (0.110 mL, 1.5 mmol), malononitrile (0.137 mmol) in DCE (1.5 mL), the additive D-CSA (2.91 mg, 0.0125 mmol) and isatin (0.125 mmol) was added at 25 °C. The reaction mixture was stirred for 24 h and quenched with saturated solution of NH_4Cl (3 mL). After extraction with ethyl acetate (3 × 10 mL) the organic layer was separated, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to give the crude Michael product. Purification by column chromatography on silica gel using hexane/ethyl acetate 7:3 as eluent gave the corresponding Michael adduct in 80% yield. The enantiomeric excess of the products was determined using Diacel Chiralpak AD-H.

Procedure for synthesis of spirooxindole [3].

To a stirred solution of **4a** (63 mg, 0.25 mmol) in ethanol (2.5 mL) $NaBH_4$ (28.5 mg, 0.75 mmol) was added. The reaction mixture was stirred for 2 h at rt and quenched with saturated solution of NH_4Cl (5 mL). After extraction with ethyl acetate the organic layer was separated, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to obtain the crude product **6**. Purfication by column chromatography on silica gel using hexane/ethyl acetate 6:4 as eluent gave spirooxindole product **6** in 90% yield. The diastereomeric ratio was determined by

^{1}H NMR analysis of the pure product. In order to determine the enantiomeric excess of **6**, a racemic sample of spirooxiindole **6** was prepared from racemic Michael adduct **4a** following the same procedure. The enantiomeric excess of spiroxindole **6** was determined using Diacel Chiralpak AD-H column and found to be 98% ee.

2-[(*S*)-2'-Oxo-3'-(2''-oxoprop-1''-yl)indolin-3'-yl]malononitrile (4a)

Sticky solid; yield = 92%; $[\alpha]_D^{25}$ = +24 (c 0.1, MeOH); ee = 99% determine by HPLC [Diacel chiralpak AD-H, hexane/*i*-PrOH, 80:20, 1.0 mL/min, λ = 254 nm, t_R (minor) = 10.2 min, t_R (major) = 13.8 min)]; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.03 (s, 3H, CH_3), 3.27 (d, J = 18.3 Hz, 1H, CH_2), 3.60 (d, J = 18.3 Hz, 1H, CH_2), 5.53 (s, 1H, CH), 6.92 (d, J = 8.1 Hz, 1H, ArH), 6.98-7.03 (m, 1H, ArH), 7.26-7.37 (m, 2H, ArH), 11.00 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 29.5, 29.6, 45.4, 48.4, 109.8, 111.3, 111.6, 123.8, 125.8, 128.6, 129.8, 142.1, 175.1, 203.6; m/z (ESI-TOF): 276.0796 (M^++Na).

2-[(*S*)-5'-Fluoro-2'-oxo-3'-(2''-oxoprop-1''-yl)indolin-3'-yl]malononitrile (4b)

Sticky solid; yield = 93%; $[\alpha]_D^{25}$ = +28 (c 0.1, MeOH); ee = 98% determined by HPLC [Diacel Chiralpak AS-H; hexane/*i*-PrOH 80 : 20; flow rate 1 mL/min; λ = 254 nm; t_R (major) = 19.1 min, t_R (major) = 50.4 min]; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.05 (s, 3H, CH_3), 3.30 (d, J = 18.3 Hz, 1H, CH_2), 3.65 (d, J = 18.3 Hz, 1H, CH_2), 5.54 (s, 1H, CH), 6.90-6.95 (m, 1H, ArH), 7.11-7.16 (m, 1H, ArH), 7.27 (d, J = 6.3 Hz, 1H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 29.7, 29.9, 45.6, 48.6, 111.0, 111.3, 111.7, 116.1, 116.4, 128.2, 139.4, 156.2, 159.3, 175.3, 203.6; m/z (ESI-TOF): 294.0649 (M^++Na)

2-[(*S*)-5'-Chloro-2'-oxo-3'-(2''-oxoprop-1''-yl)indolin-3'-yl]malononitrile (4c)

Sticky solid; yield = 95%; $[\alpha]_D^{25}$ = +32 (c 0.1, MeOH); ee = 98% determined by HPLC [Diacel Chiralpak AS-H; hexane/*i*-PrOH 80 : 20; flow rate 1 mL/min; λ = 254 nm; t_R (major) = 20.2 min, t_R (major) = 45.1 min]; ^{1}H NMR (300 MHz, DMSO-d_6): *δ* 2.05 (s, 3H, CH_3), 3.31 (d, J = 18.3 Hz, 1H, CH_2), 3.68 (d, J = 18.3 Hz, 1H, CH_2), 5.55 (s, 1H, CH), 6.94 (d, J = 8.1 Hz, 1H, ArH), 7.33-7.45 (m, 2H, ArH), 11.12 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): *δ* 29.6, 29.8, 45.6, 48.4, 111.0, 111.3, 111.5, 123.8, 125.8, 128.6, 129.8, 142.1, 175.1, 203.6; m/z (ESI-TOF): 310.0349 (M^++Na).

2-[(*S*)-5'-Bromo-2'-oxo-3'-(2''-oxoprop-1''-yl)indolin-3'-yl]malononitrile (4d)

Sticky solid; yield = 94%; $[\alpha]_D^{25}$ = +28 (c 0.1, MeOH); ee = 98% determined by HPLC [Diacel Chiralpak AS-H; hexane/*i*-PrOH 70 : 30; flow rate 1 mL/min; λ = 254 nm; t_R (major) = 11.5 min, t_R (minor) = 23.5 min]; ^{1}H NMR (300 MHz, DMSO-d_6): *δ* 2.05 (s, 3H, CH_3), 3.32 (d, J = 18.0 Hz, 1H, CH_2), 3.68 (d, J = 18.0 Hz, 1H, CH_2), 5.55 (s, 1H, CH), 6.89 (d, J = 8.4 Hz, 1H, ArH), 7.46-7.57 (m, 2H, ArH), 11.13 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): *δ* 29.6, 29.8, 45.6, 48.3, 110.9, 111.3, 112.0, 113.4, 126.5, 128.9, 132.6, 142.5, 175.0, 203.7; m/z (ESI-TOF): 353.9842 (M^++Na).

2-[(*S*)-5'-Iodo-2'-oxo-3'-(2''-oxoprop-1''-yl)indolin-3'-yl]malononitrile (4e)

Sticky solid; yield = 91%; $[\alpha]_D^{25}$ = +21 (c 0.1, MeOH); ee = 99% determined by HPLC [Diacel Chiralpak AS-H; hexane/*i*-PrOH 70 : 30; flow rate 1 mL/min; λ = 254 nm; t_R (major) = 12.1 min, t_R (minor) = 23.5 min]; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.05 (s, 3H, CH_3), 3.29 (d, J = 18.3 Hz, 1H, CH_2), 3.67 (d, J = 18.3 Hz, 1H, CH_2), 5.54 (s, 1H, CH), 6.78 (d, J = 8.1 Hz, 1H, ArH), 7.62-7.69 (m, 2H, ArH); 11.25 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): *δ* 29.6, 29.8, 45.6, 48.1, 84.6, 111.0, 111.3, 112.4, 129.2, 131.8, 138.4, 142.9, 174.8, 203.7; m/z (ESI-TOF): 401.9715 (M^++Na).

2-[(*S*)-5',7'-Dibromo-2'-oxo-3'-(2''-oxoprop-1''-yl)indolin-3'-yl]malononitrile (4f)

Sticky solid; yield = 92%; $[\alpha]_D^{25}$ = +51 (c 0.1, MeOH); ee = 96% determined by HPLC [Diacel Chiralpak AD-H; hexane/*i*-PrOH 90 : 10; flow rate 1 mL/min; λ = 254 nm; t_R (minor) = 22.4 min, t_R (major) = 30.9 min]; ^{1}H NMR (300 MHz, DMSO-d_6): *δ* 2.06 (s, 3H, CH_3), 3.37 (d, J = 18.3 Hz, 1H, CH_2), 3.73 (d, J = 18.3 Hz, 1H, CH_2), 5.60 (s, 1H, CH), 7.60 (s, 1H, ArH), 7.77 (s, 1H, ArH), 11.49 (s, 1H, NH); ^{13}C NMR (75 MHz; DMSO-d_6): *δ* 29.5, 29.8, 45.8, 49.2, 103.1, 110.7, 111.0, 113.9, 125.7, 130.0, 134.6, 142.2, 174.8, 203.8; m/z (ESI-TOF): 431.9015 (M^++Na).

2-[(*S*)-1'-Allyl-5'-chloro-2'-oxo-3'-(2''-oxoprop-1''-yl)indolin-3'-yl]malononitrile (4g)

Sticky solid; yield = 85%; $[\alpha]_D^{25}$ = +38 (c 0.1, MeOH); ee = 89% determined by HPLC [Diacel Chiralpak AS-H; hexane/*i*-PrOH 80 : 20; flow rate 1 mL/min; λ = 254 nm; t_R (major) = 10.7 min, t_R (minor) = 25.4 min]; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 2.08 (s, 3H, CH_3), 3.12 (d, J = 18.0 Hz, 1H, CH_2), 3.42 (d, J = 18.0 Hz, 1H, CH_2), 4.35-4.437 (m, 3H, NCH_2 and CH), 5.22-5.38 (m, 2H, CH=C*H*$_2$), 5.74-5.84 (m, 1H, C*H*=CH$_2$), 6.84 (d, J = 8.4 Hz, 1H, ArH), 7.29-7.37 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 30.7, 30.9, 44.7, 47.3, 49.6, 109.7, 110.8, 112.1, 124.5, 127.2, 129.7, 131.4, 142.9, 173.6, 202.9; m/z (ESI-TOF): 350.0654 (M^++Na).

2-[(*S*)-1'-Allyl-5'-bromo-2'-oxo-3'-(2''-oxoprop-1''-yl)indolin-3'-yl]malononitrile (4h)

Sticky solid; yield = 87%; $[\alpha]_D^{25}$ = +35 (c 0.1, MeOH); ee = 92% determined by HPLC [Diacel Chiralpak AS-H; hexane/*i*-PrOH 80 : 20; flow rate 1 mL/min; λ = 254 nm; t_R (major) = 12.8 min, t_R (minor) = 37.9 min]; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 2.14 (s, 3H, CH_3), 3.20 (d, J = 18.3 Hz, 1H, CH_2), 3.49 (d, J = 18.3 Hz, 1H, CH_2), 4.40-4.42

(m, 2H, NCH_2), 4.46 (s, 1H, CH), 5.28-5.45 (m, 2H, $CH=CH_2$), 5.80-5.90 (m, 1H, $CH=CH_2$), 6.86 (d, J = 8.4 Hz, 1H, ArH), 7.51-7.57 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.9, 30.1, 43.2, 46.6, 48.8, 109.1, 110.1, 111.8, 116.1, 118.7, 126.4, 126.9, 130.0, 133.6, 142.7, 172.8, 202.3; m/z (ESI-TOF): 396.0134 (M^++Na+2H).

2-[(*S*)-1'-Benzyl-2'-oxo-3'-(2''-oxoprop-1''-yl)indolin-3'-yl]malononitrile (4i)

Sticky solid; yield = 86%; $[\alpha]_D^{25}$ = +45 (c 0.1, MeOH); ee = 88% determined by HPLC [Diacel Chiralpak AS-H; hexane/*i*-PrOH 80 : 20; flow rate 1 mL/min; λ = 254 nm; t_R (major) = 10.8 min, t_R (minor) = 16.1 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15 (s, 3H, CH_3), 3.18 (d, J = 17.7 Hz, 1H, CH_2), 3.53 (d, *J* = 17.7 Hz, 1H, CH_2), 4.53 (s, 1H, CH), 5.01 (br s, 2H, CH_2), 6.81 (d, J = 8.1 Hz, 1H, ArH), 7.08-7.17 (m, 2H, ArH), 7.25-7.47 (m, 6H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.1, 30.2, 44.7, 46.5, 48.9, 109.4, 110.4, 110.5, 123.3, 123.6, 124.9, 127.3, 127.8, 128.8, 130.7, 134.6, 143.5, 173.7, 202.5; m/z (ESI-TOF): 366.1236 (M^++Na).

2-[(*S*)-2'-Oxo-3'-(4''-methyl-2''-oxopent-1''-yl)indolin-3'-yl]malononitrile (4j)

Sticky solid; yield = 80%; $[\alpha]_D^{25}$ = +45 (c 0.1, MeOH); ee = 96% determined by HPLC [Diacel Chiralpak IB; hexane/*i*-PrOH 90 : 10; flow rate 1 mL/min; λ = 254 nm; t_R (major) = 27.2 min, t_R (minor) = 16.7 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (d, J = 10.5 Hz, 6H, 2 × CH_3), 1.98-2.08 (m, 1H, CH), 2.25-2.28 (m, 2H, CH_2), 3.14 (d, J = 17.7 Hz, 1H, CH_2), 3.45 (d, J = 18.0 Hz, 1H, CH_2), 4.56 (s, 1H, CH), 6.99-7.14 (m, 2H, ArH), 7.33-7.44 (m, 2H, ArH), 8.55 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 20.9, 24.6, 49.3, 51.8, 53.7, 60.4, 109.5, 110.4, 111.1, 123.4, 123.6, 125.5, 130.7, 141.5, 171.2, 205.4; m/z (ESI-TOF): 318.1212 (M^++Na).

2-[(*S*)-2'-Oxo-3'-(2''-oxooct-1''-yl)indolin-3'-yl]malononitrile (4k)

Sticky solid; yield = 85%; $[\alpha]_D^{25}$ = +28 (c 0.1, MeOH); ee = 97% determined by HPLC [Diacel Chiralpak AS-H; hexane/*i*-PrOH 90 : 10; flow rate 1 mL/min; λ = 254 nm; t_R (major) = 30.1 min, t_R (minor) = 25.3 min]; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 0.84 (t, J = 6.9 Hz, 1H, CH_3), 1.20-1.25 (m, 6H, CH_2), 1.45-1.52 (m, 1H, CH_2), 2.36-2.41 (m, 1H, CH_2), 3.17 (d, J = 18.0 Hz, 1H, CH_2), 3.46 (d, J = 17.4 Hz, 1H, CH_2), 4.58 (s, 1H, CH), 6.99 (d, J = 7.8 Hz, 1H, ArH), 7.08-7.13 (m, 1H, ArH), 7.32-7.43 (m, 2H, ArH), 8.78 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 13.9, 22.4, 23.4, 28.6, 29.9, 30.3, 31.5, 43.1, 45.5, 49.3, 109.7, 110.5, 111.4, 123.6, 125.7, 125.5, 130.8, 141.6, 175.7, 206.1; m/z (ESI-TOF): 346.1518 (M^++Na).

6'-Amino-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (6)

Yellow solid; yield = 90%; m.p. = 283-284 °C; $[\alpha]_D^{25}$ = +28 (c 0.1, MeOH); dr = 82:18; ee = 98% determined by HPLC [Diacel Chiralpak AD-H; hexane/*i*-PrOH 80 : 20; flow rate 1 mL/min; λ = 254 nm; t_R (major) = 13.8 min, t_R (minor) = 12.1 min]; ^{1}H NMR (300 MHz, acetone-d_6): *δ* 1.32 (d, J = 7.8 Hz, 3H, CH_3), 1.69-1.74 (m, 1H, CH_2), 1.81-1.86 (m, 1H, CH_2), 4.56-4.64 (m, 1H, CH), 5.89 (s, 2H, NH_2), 6.94-7.03 (m, 2H, ArH), 7.20-7.25 (m, 1H, ArH), 7.39 (d, J = 6.0 Hz, 1H, ArH), 9.51 (s, 1H, NH); ^{13}C NMR (75 MHz, acetone-d_6): *δ* 20.9, 40.0, 48.7, 56.2, 71.8, 110.5, 119.7, 122.8, 124.9, 129.2, 135.8, 141.9, 166.5, 179.8; m/z (ESI-TOF): 278.0915 (M^++Na).

References

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[2] For synthesis of Primary-tertiary diamines, see: Kumar, A.; Singh, S.; Kumar, V.; Chimni, S. S. *Org. Biomol. Chem.* **2011**, *9*, 2731-2742.

[3] For preparation of spirooxindoles, see: Liu, L.; Wu, D.; Li, X.; Wang, S.; Li, H.; Li, J.; Wang, W. *Chem. Commun.* **2012**, *48*, 1692-1694;

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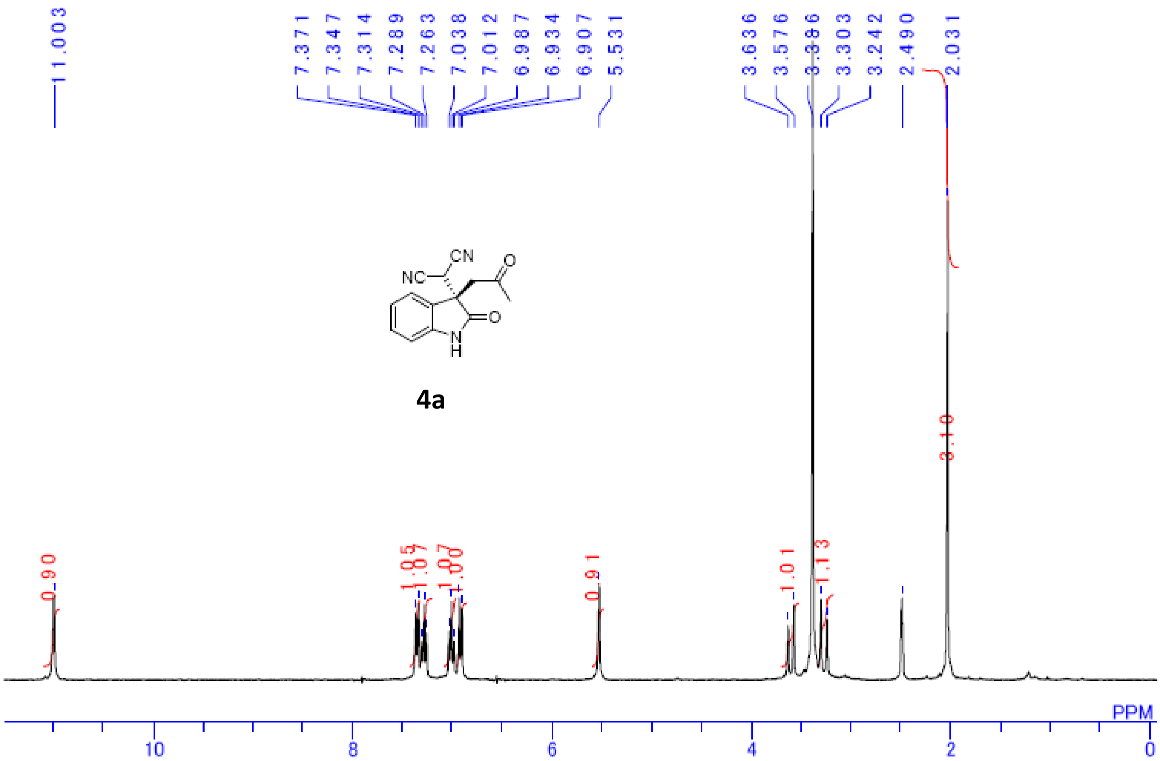

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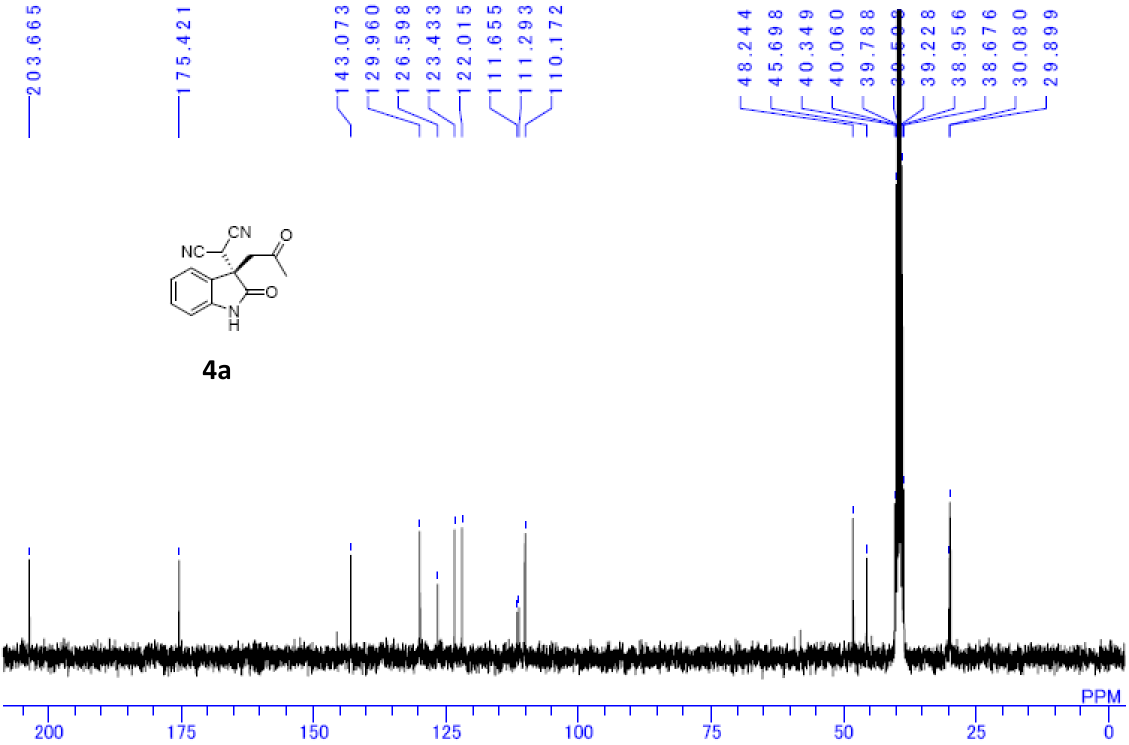

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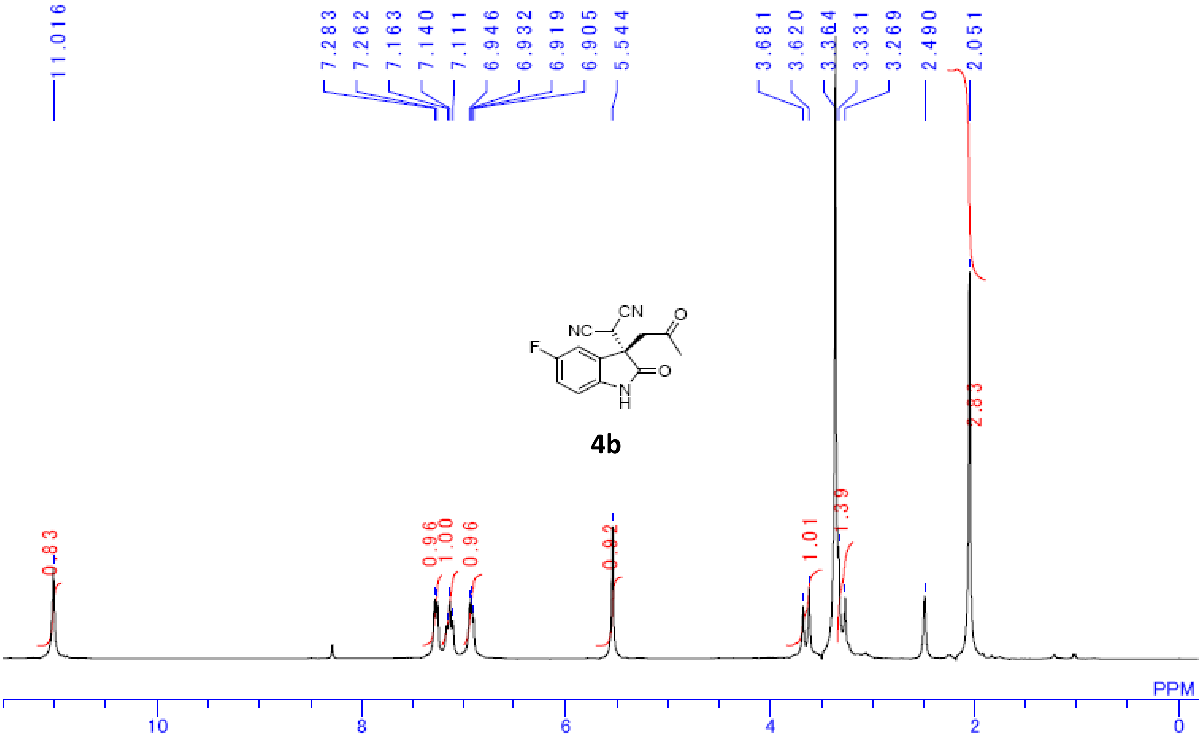

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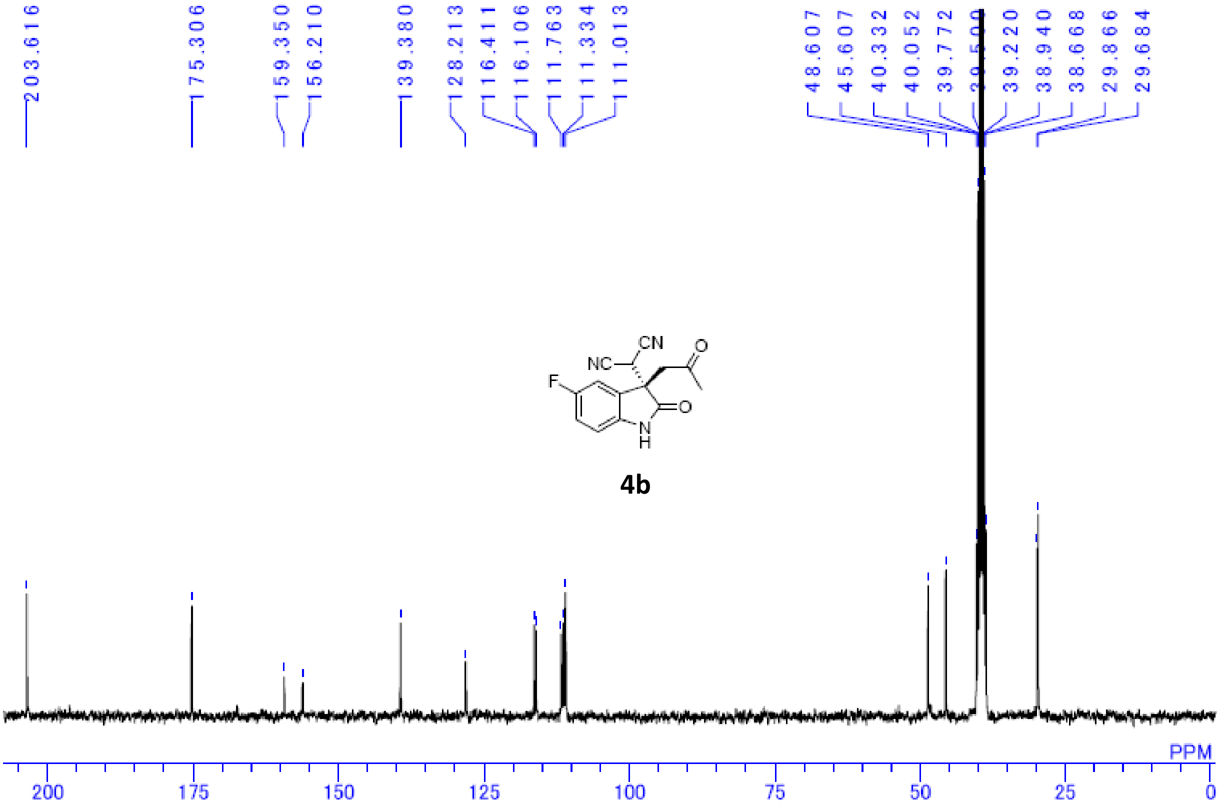

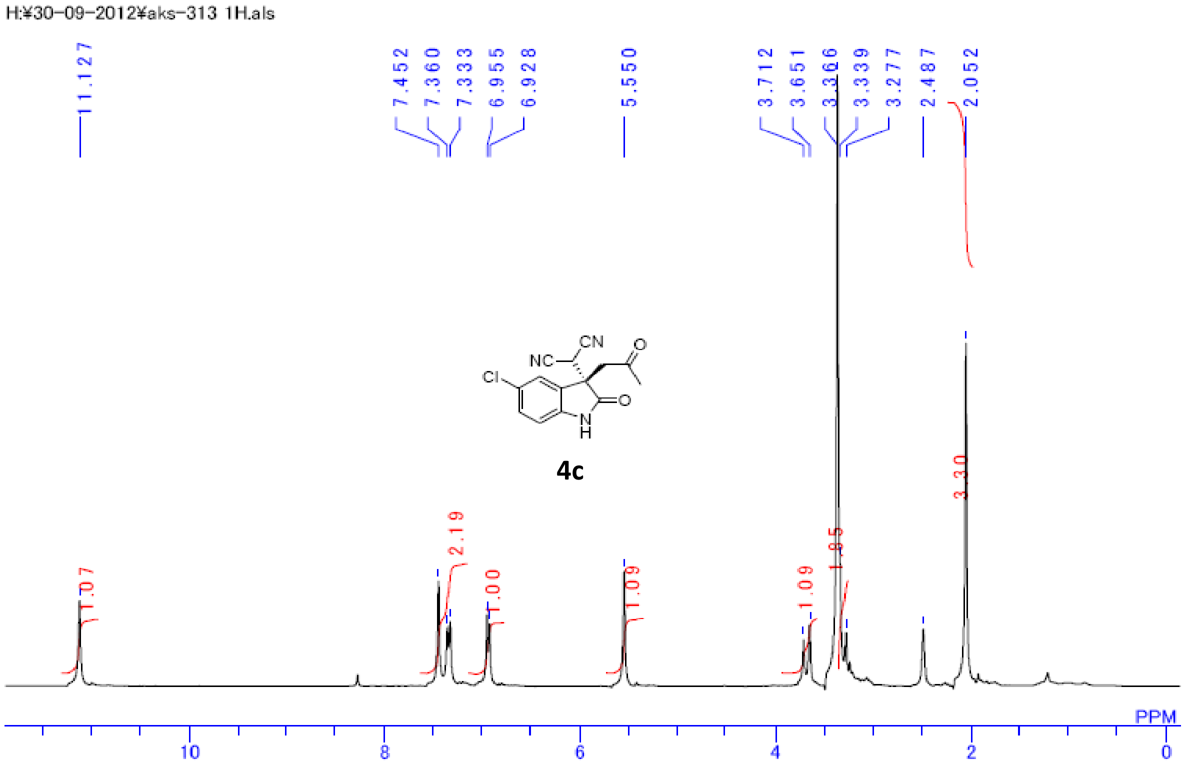
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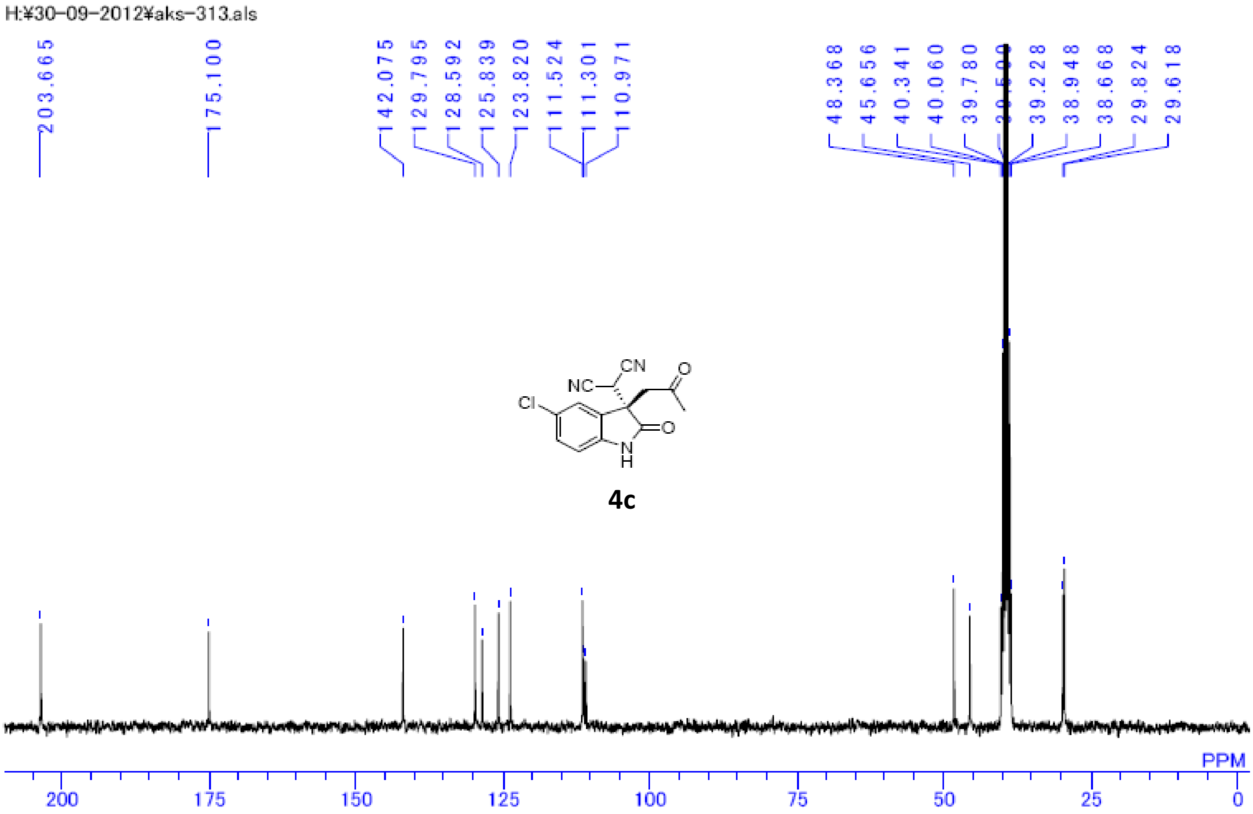
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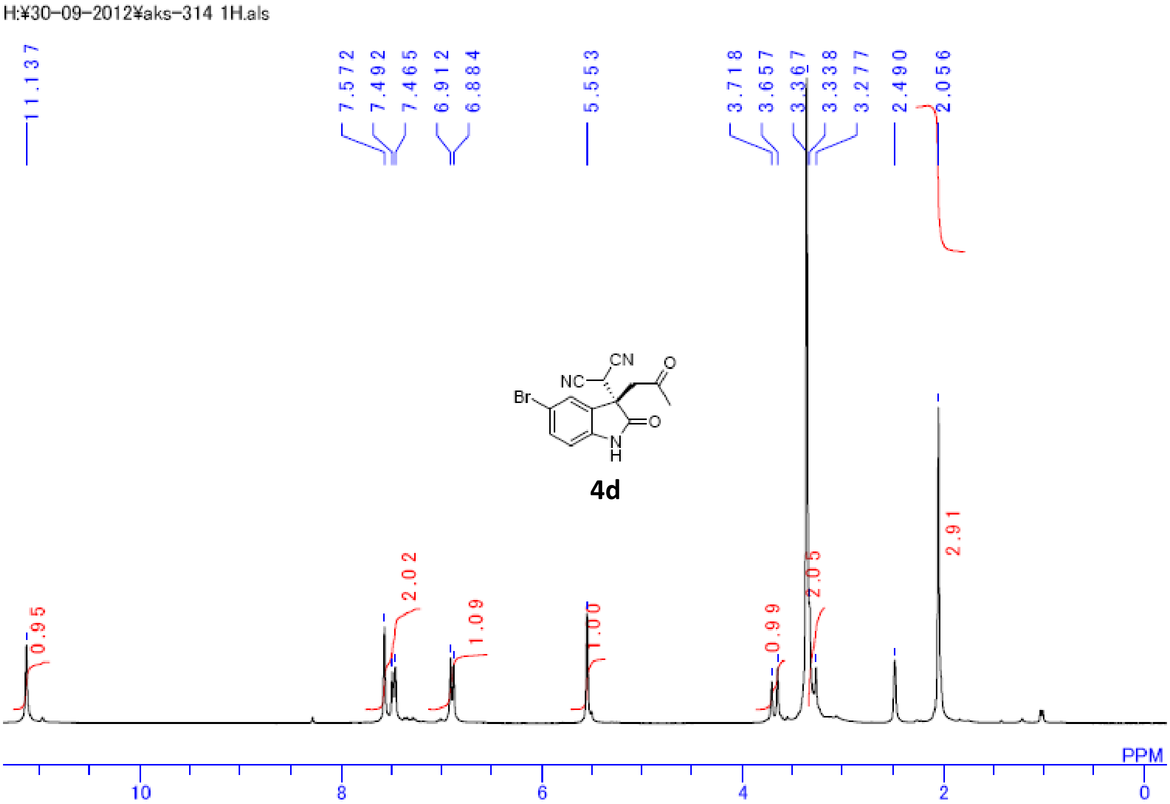
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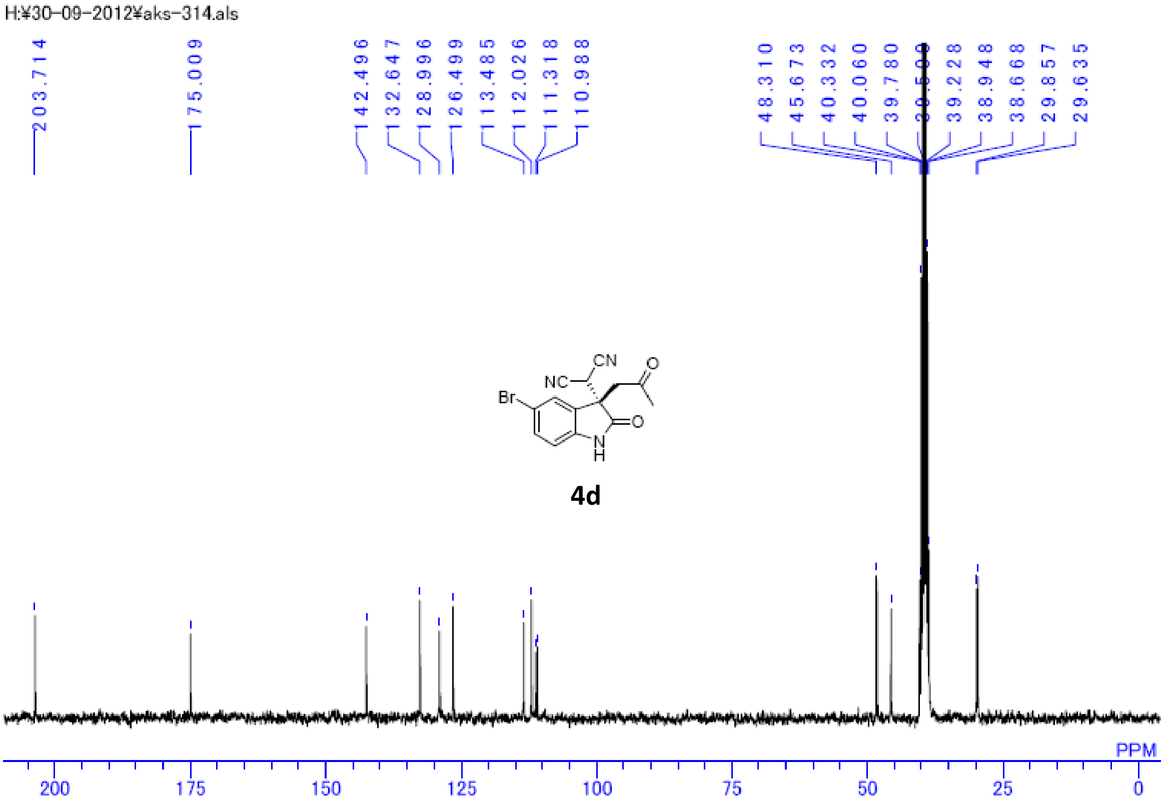
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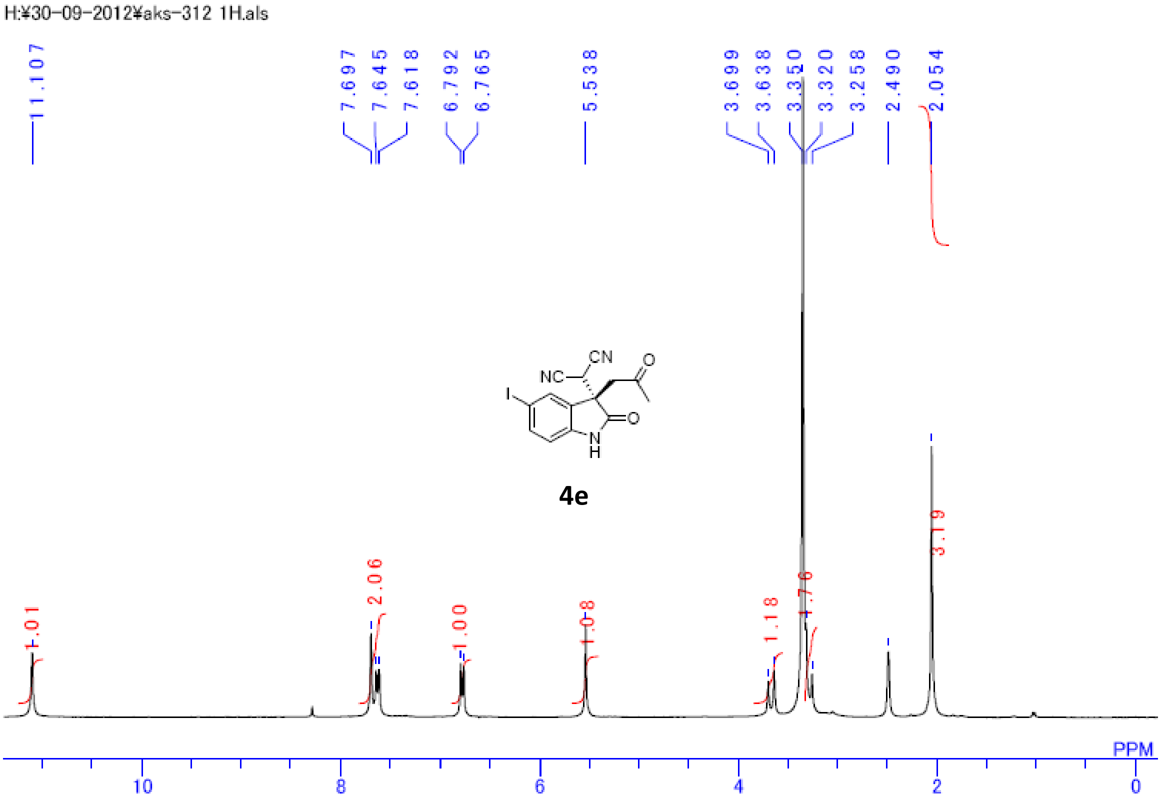
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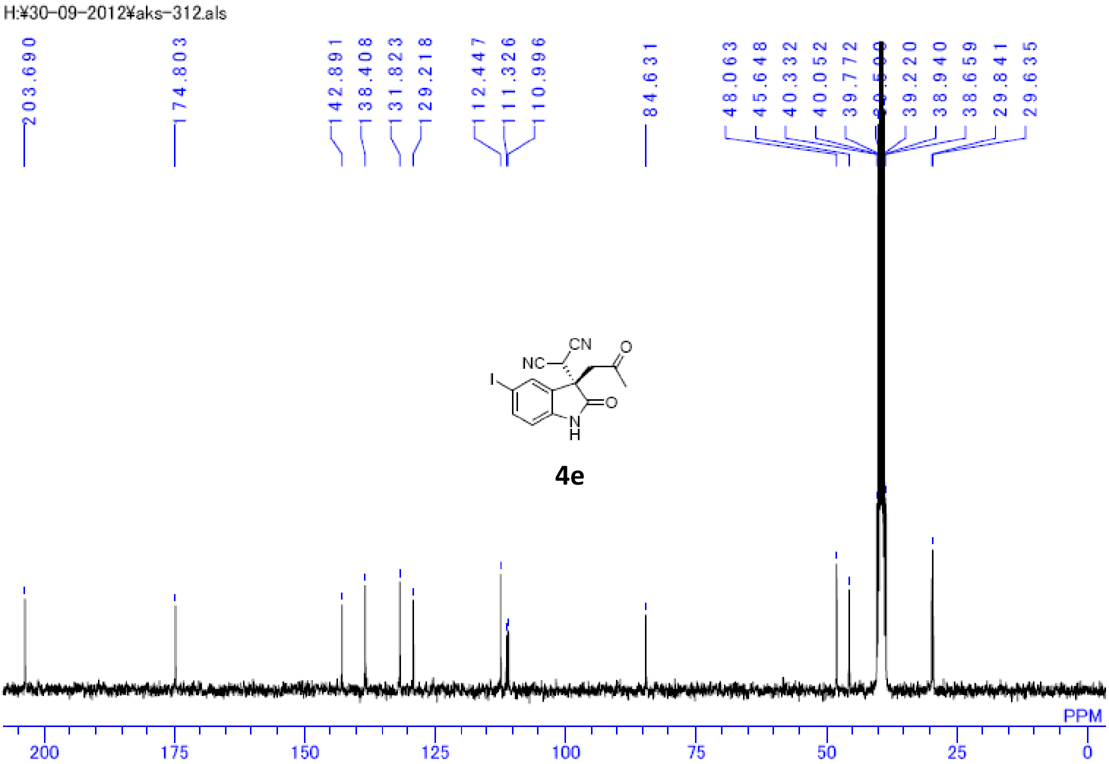
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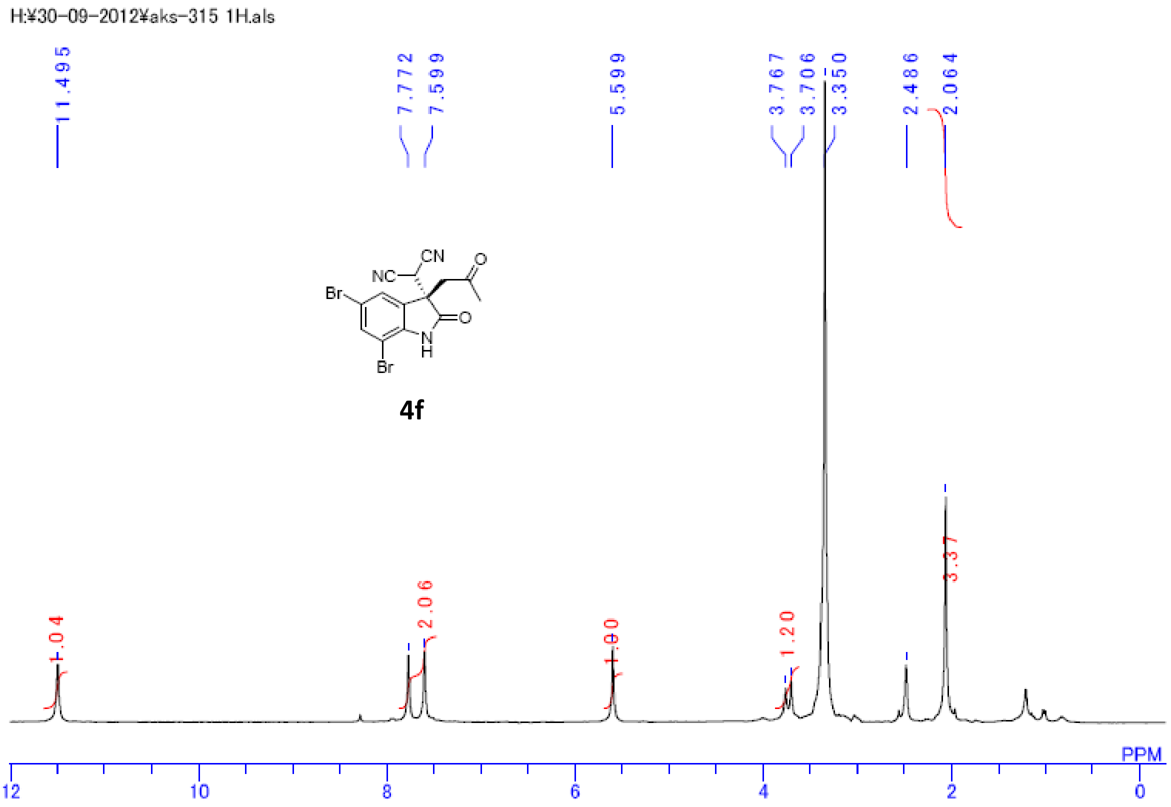
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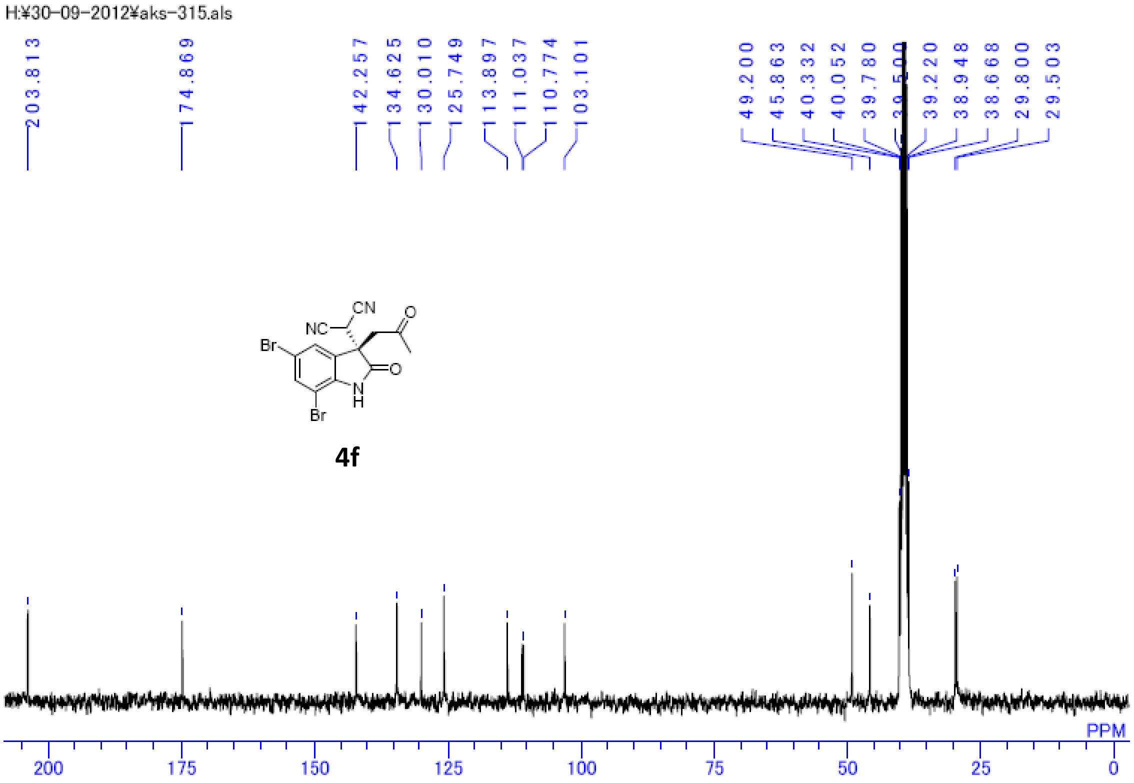
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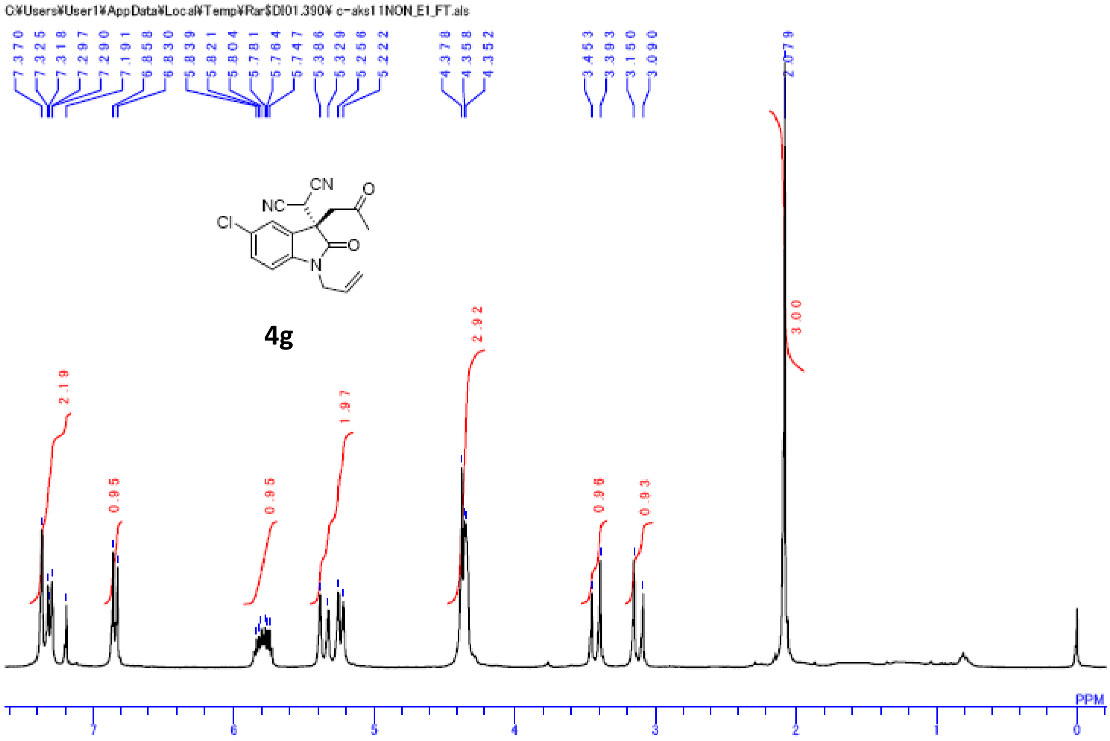
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O
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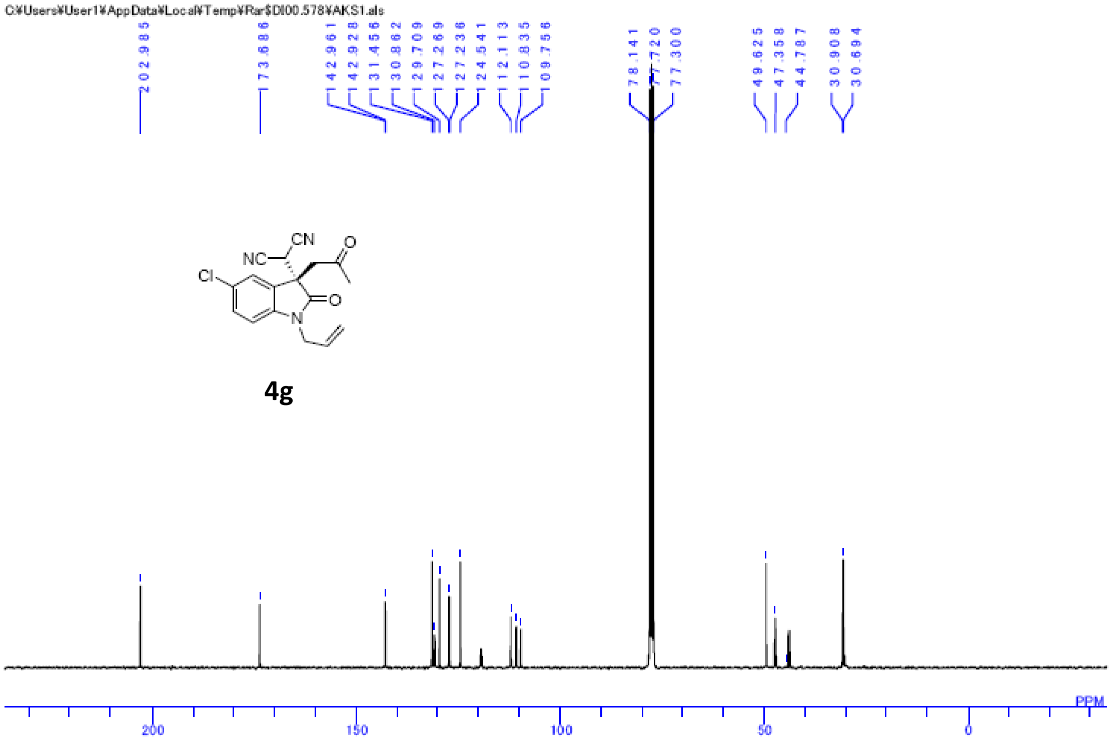
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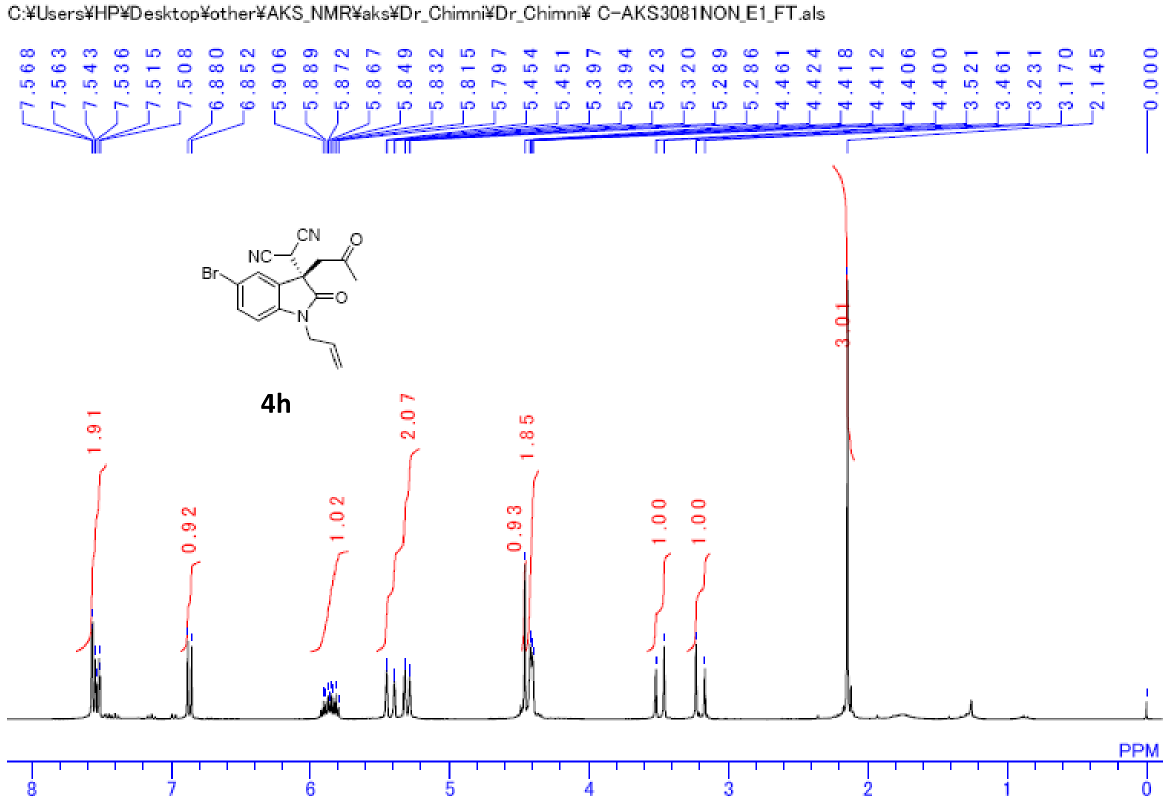
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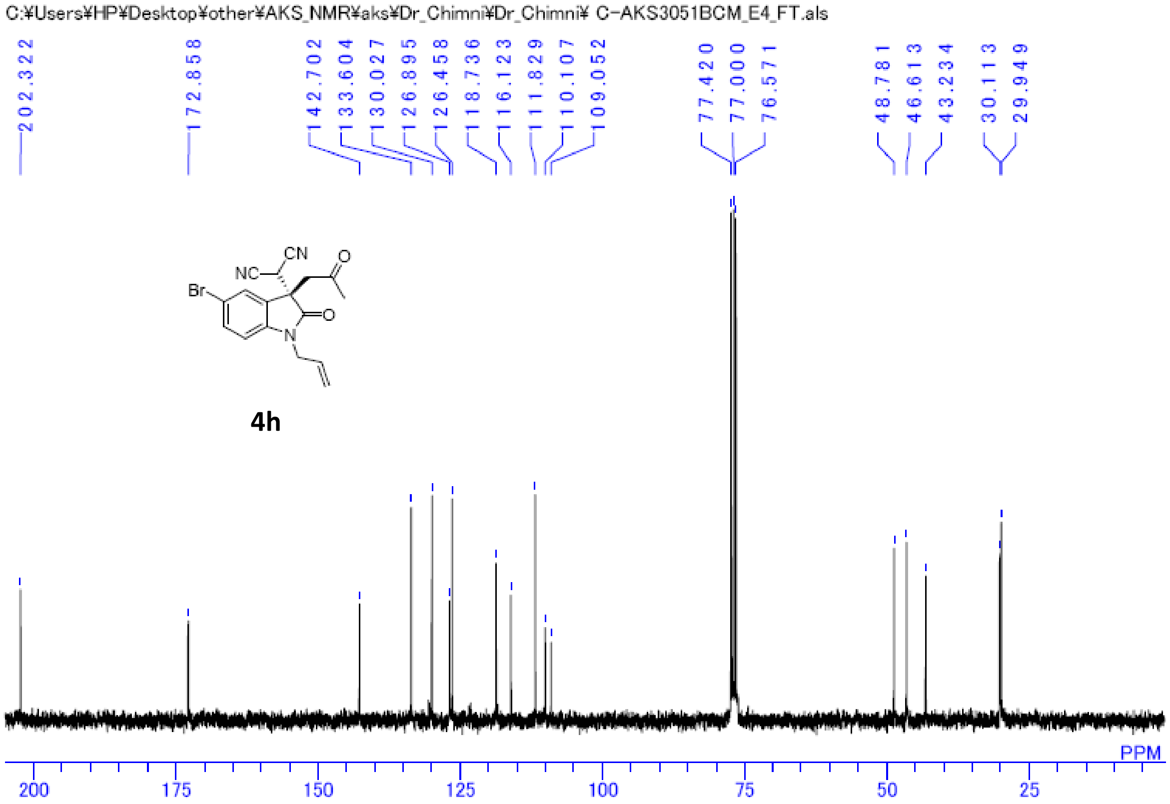
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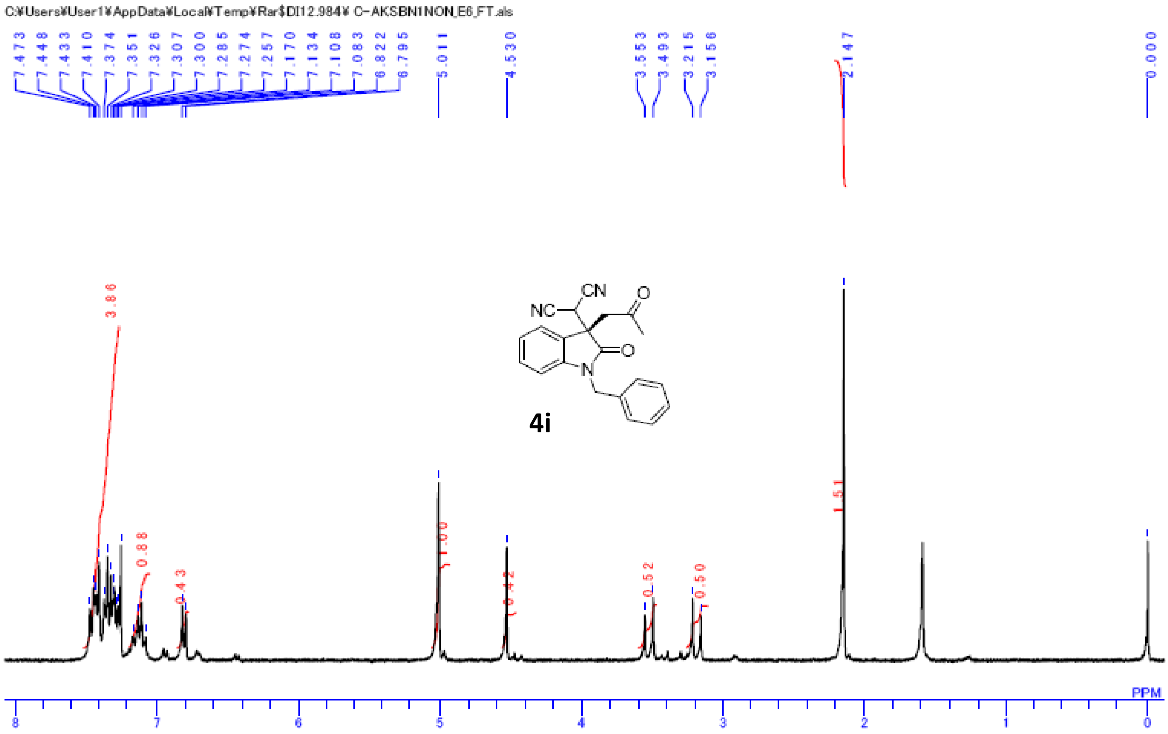
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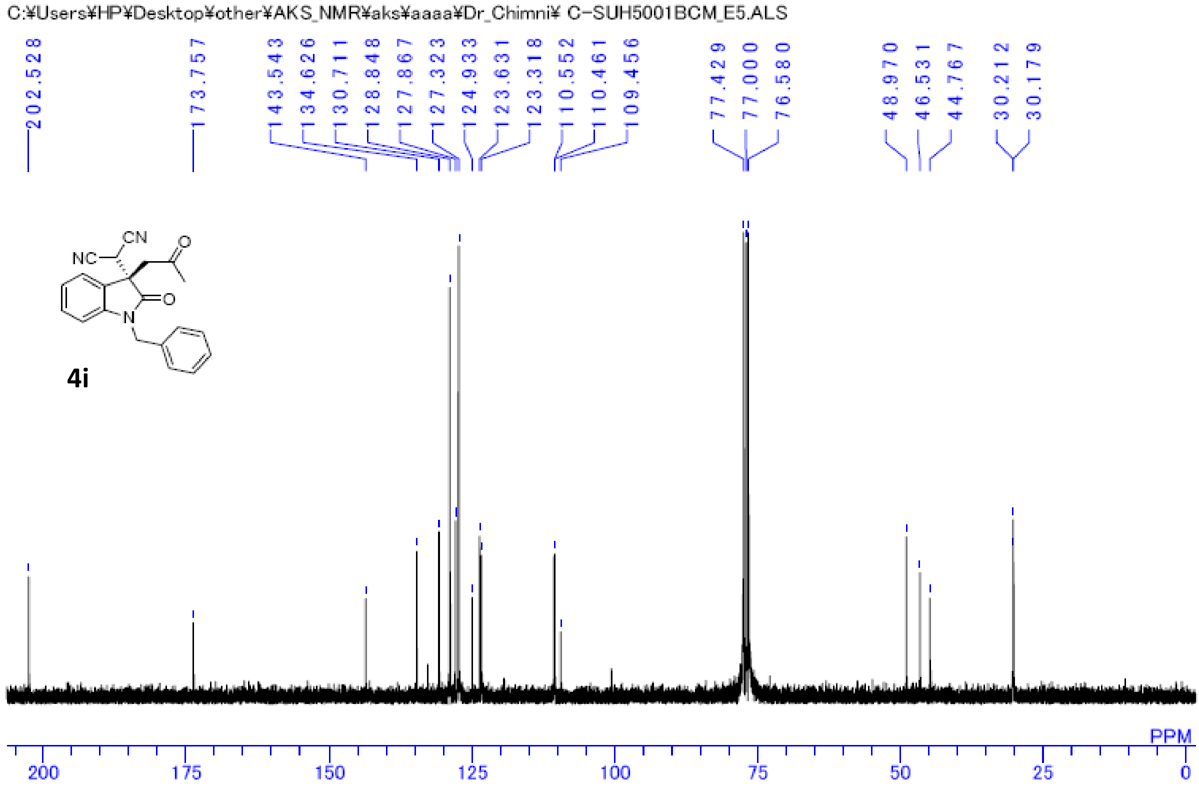
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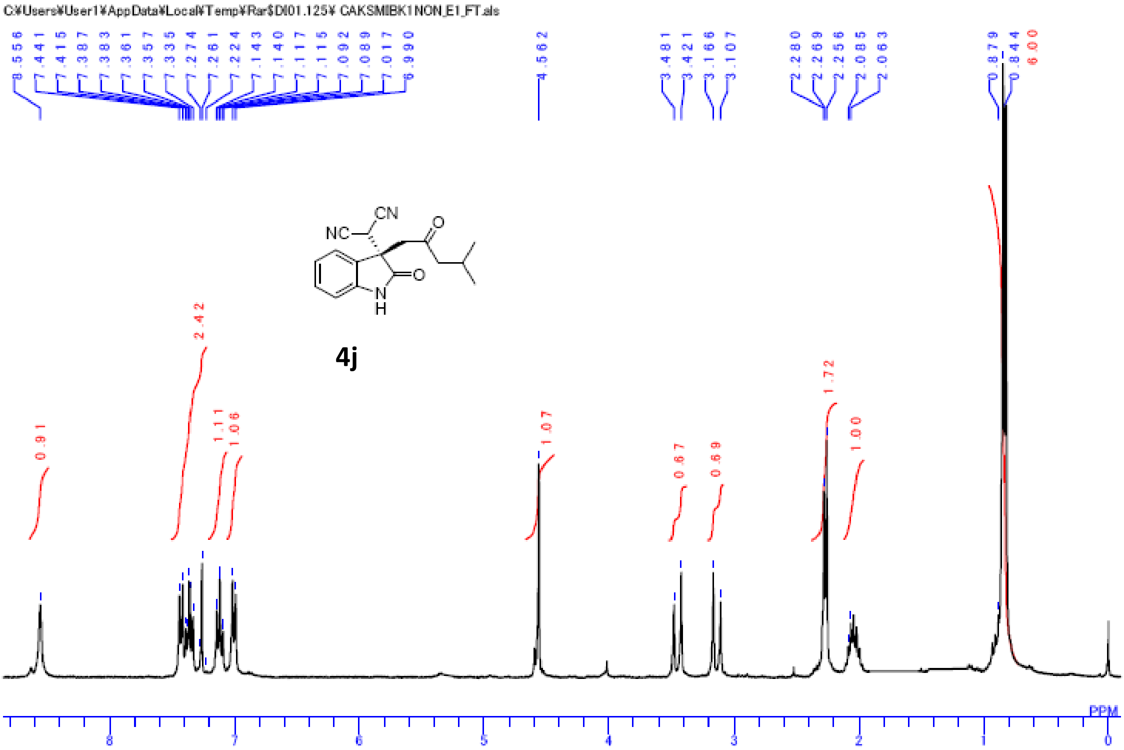
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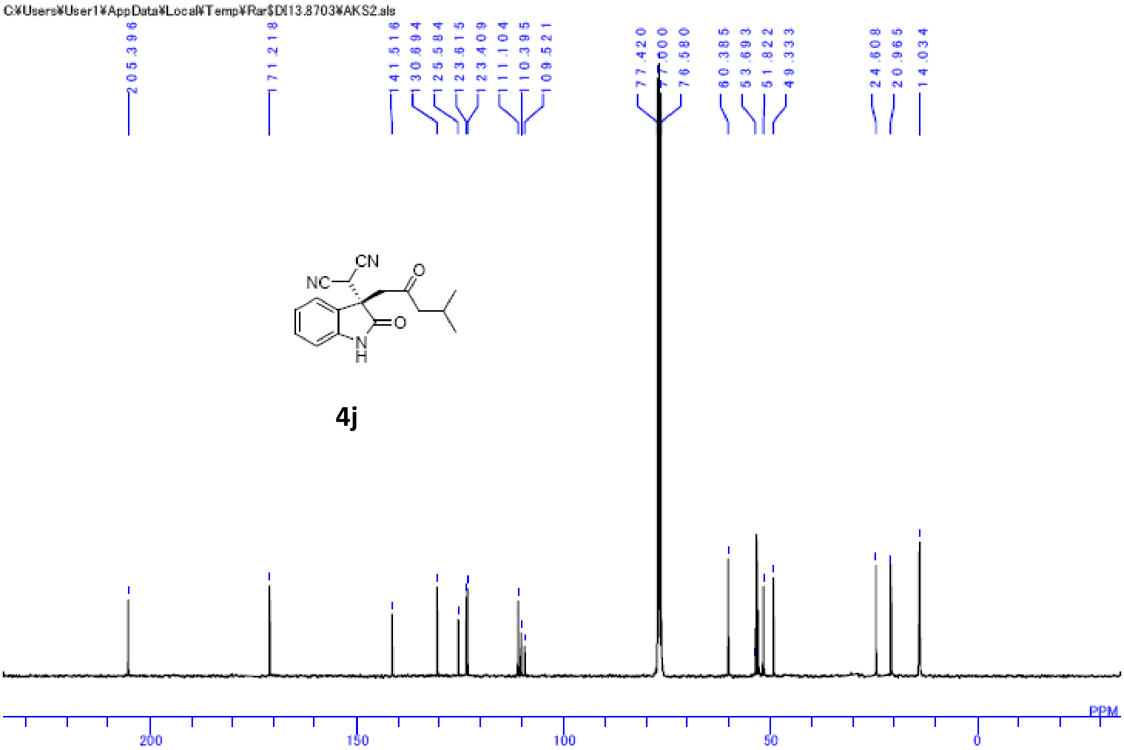
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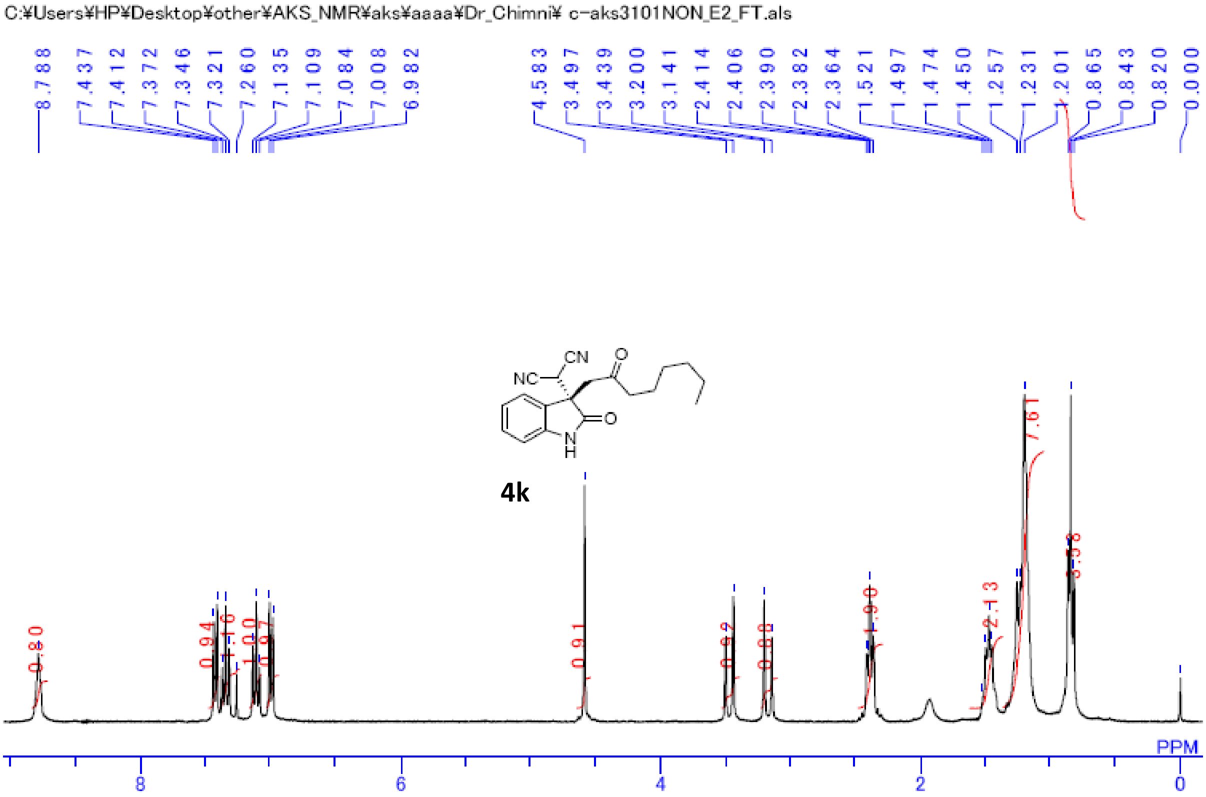
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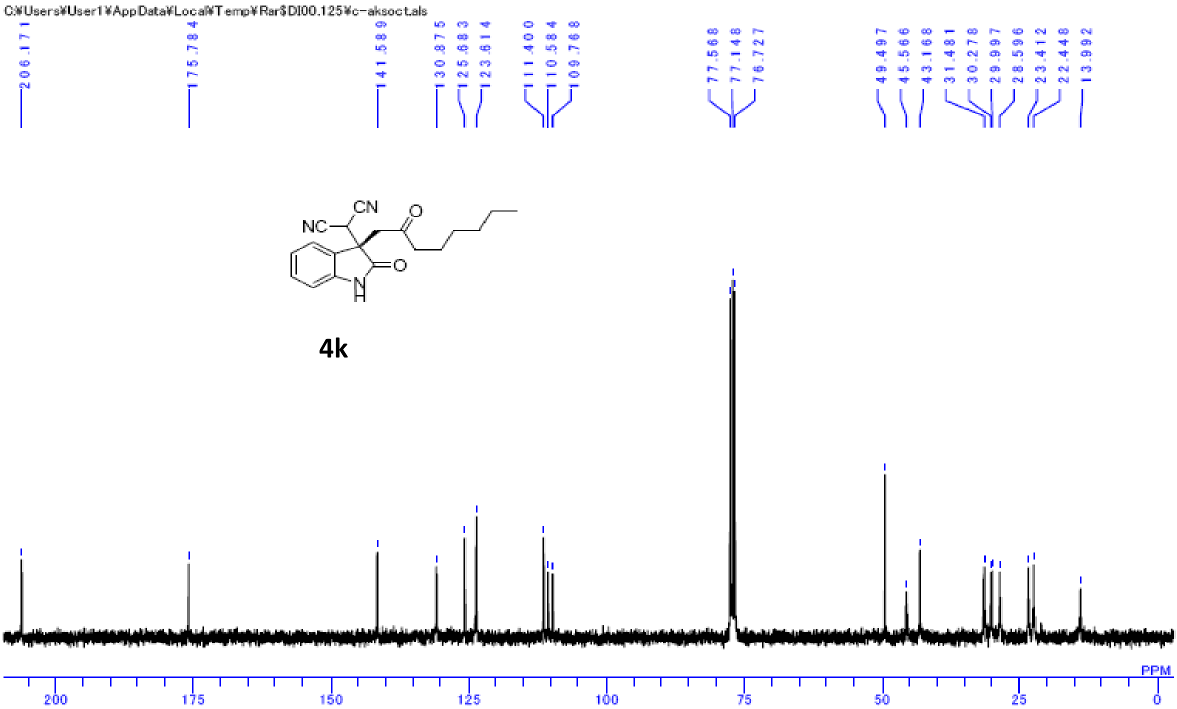
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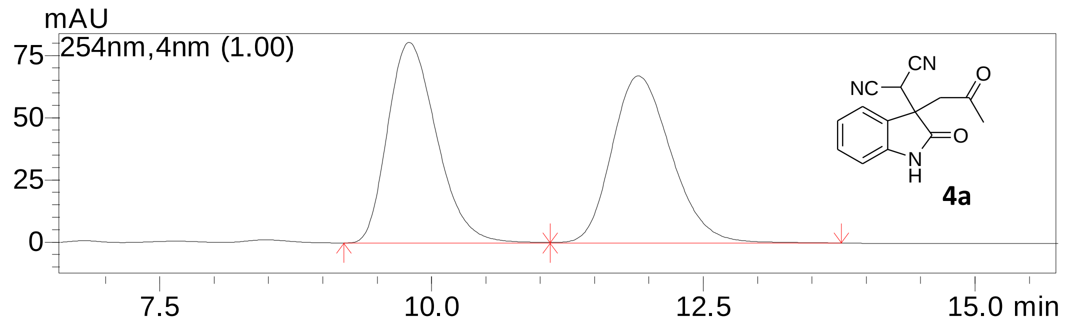
4k



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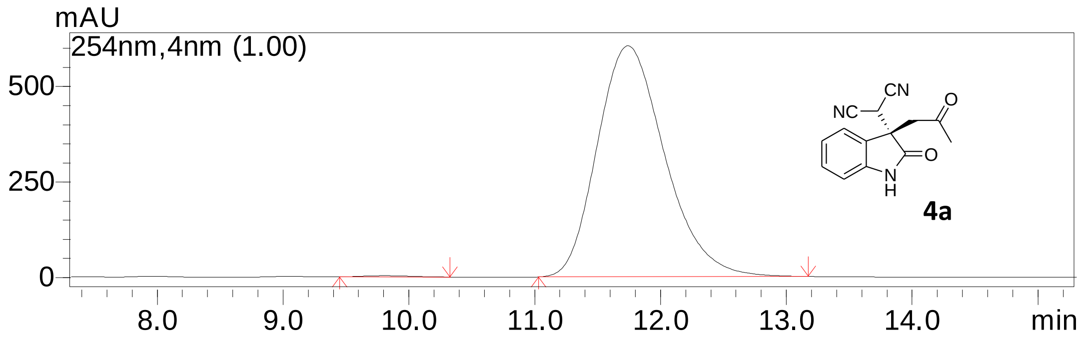

Entry	Ret. Time	Area%
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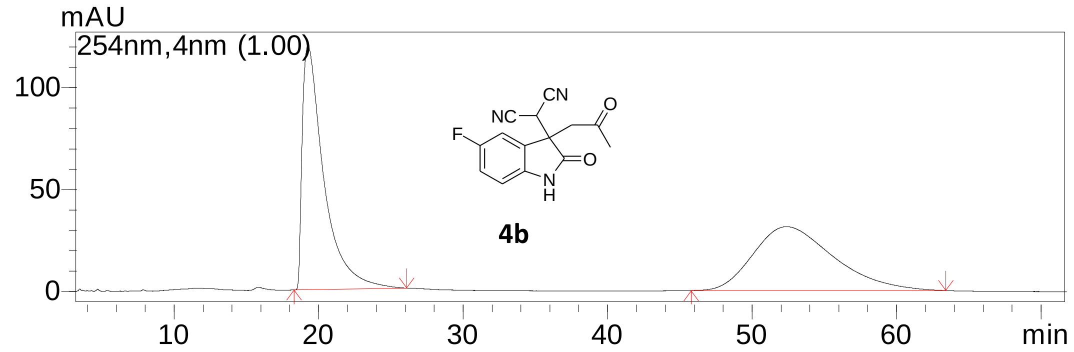

Peak	Ret. Time	Area%
1	19.252	50.6597
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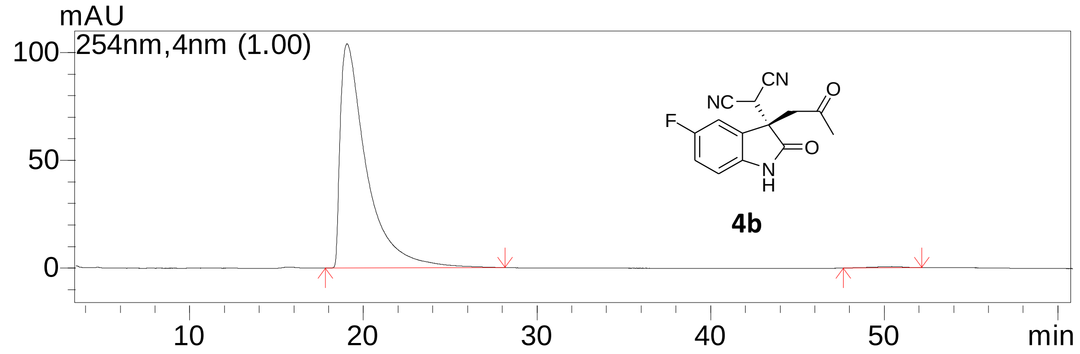

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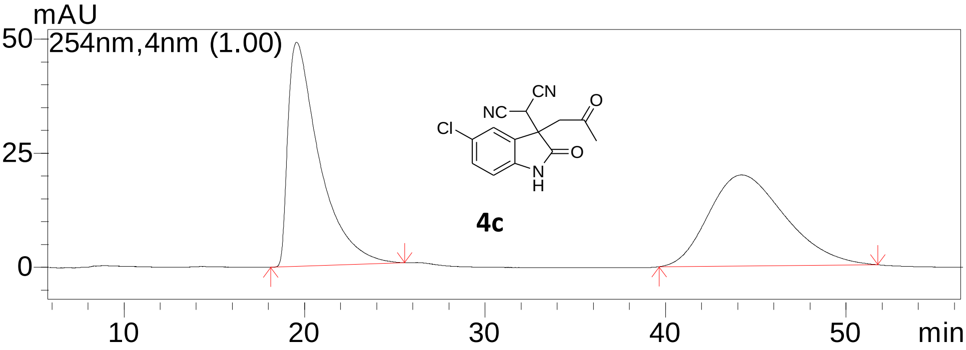

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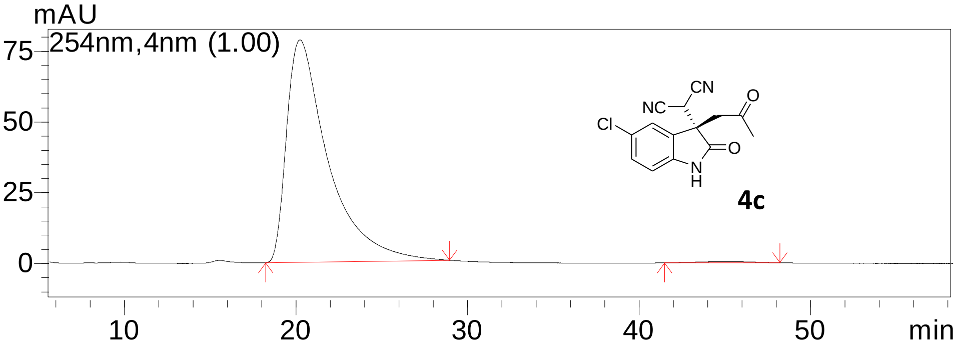

Peak	Ret. Time	Area%
1	20.227	99.2792
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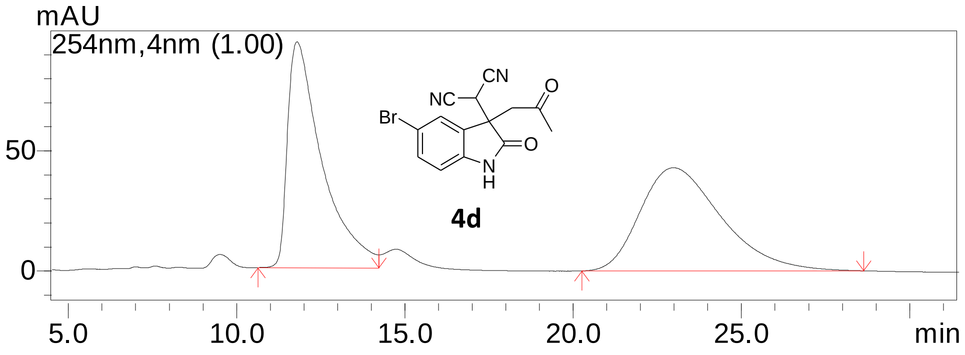

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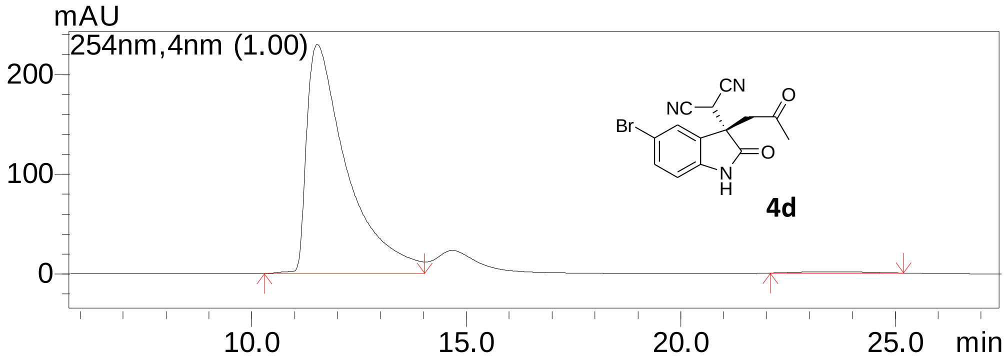

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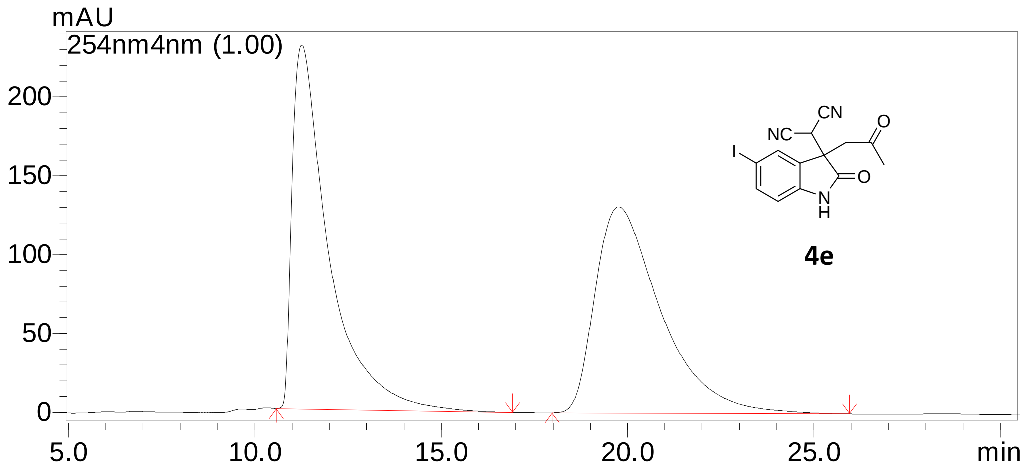

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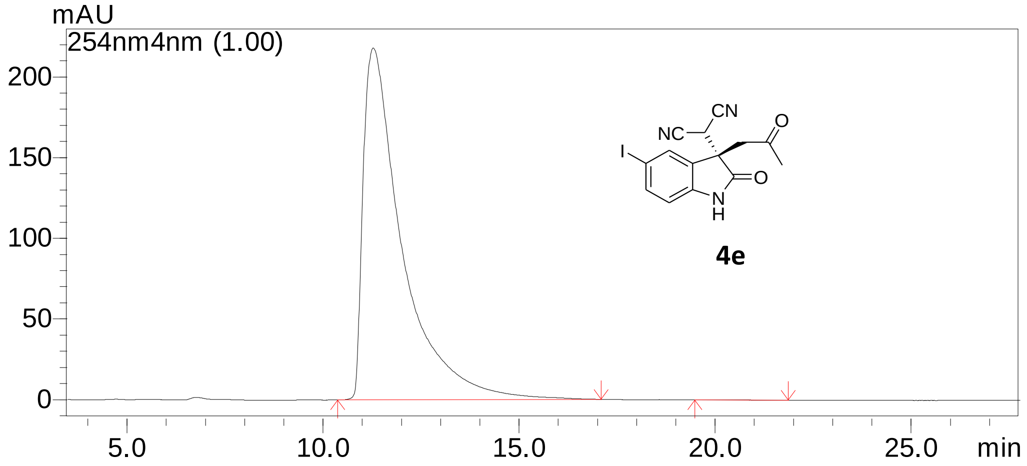

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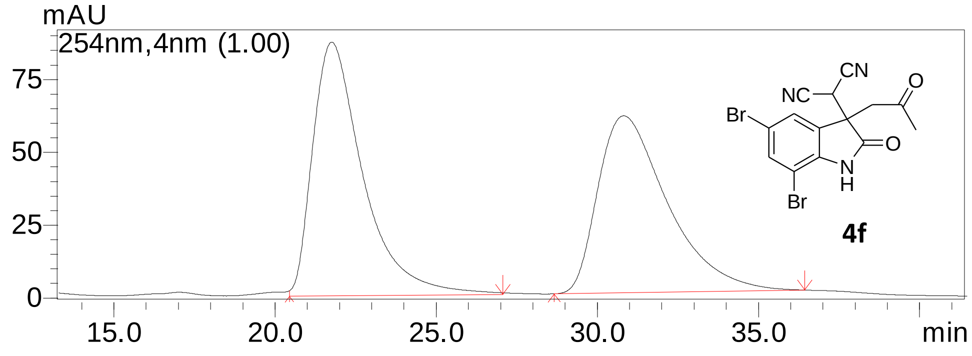

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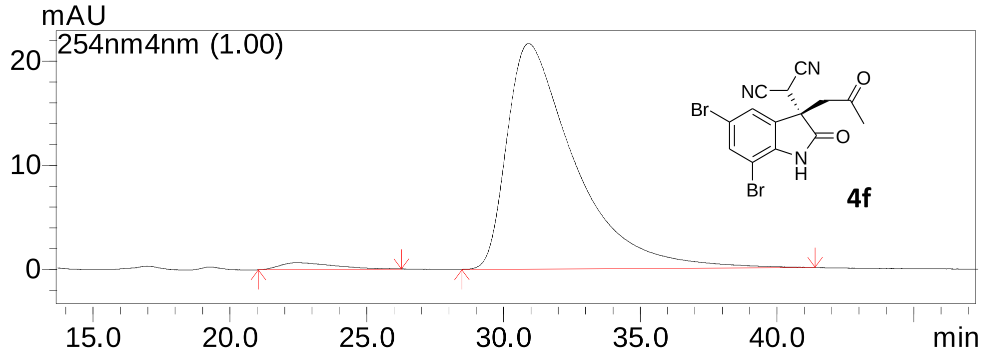

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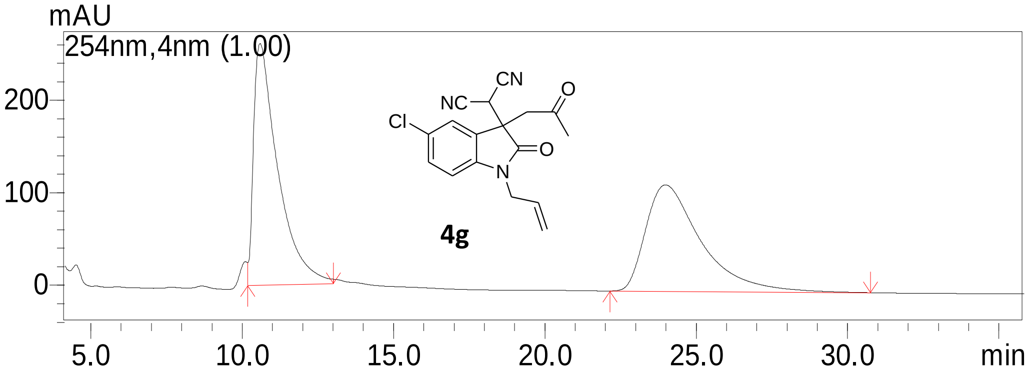

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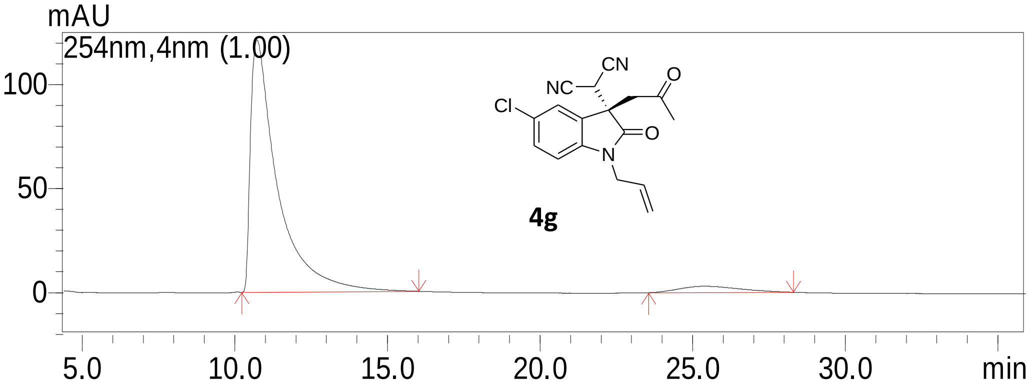

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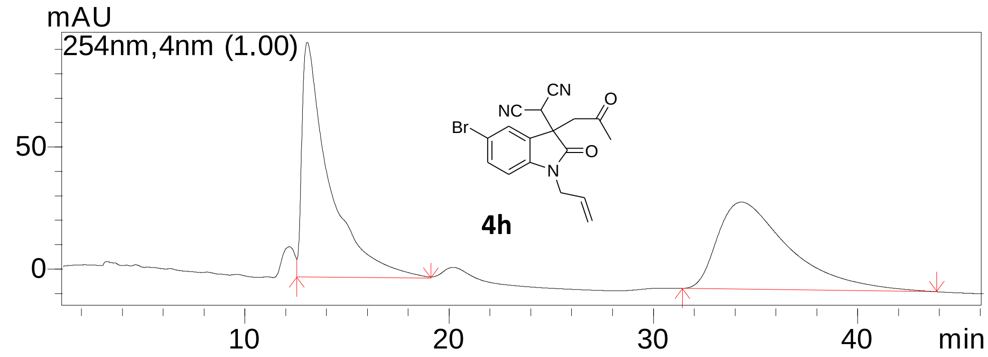

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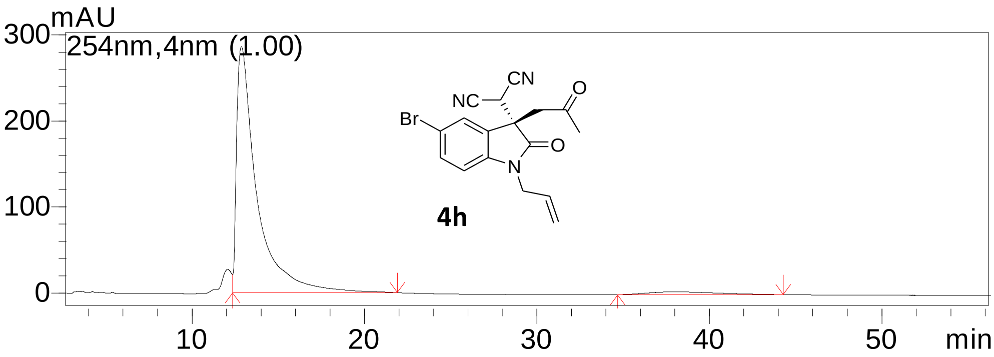

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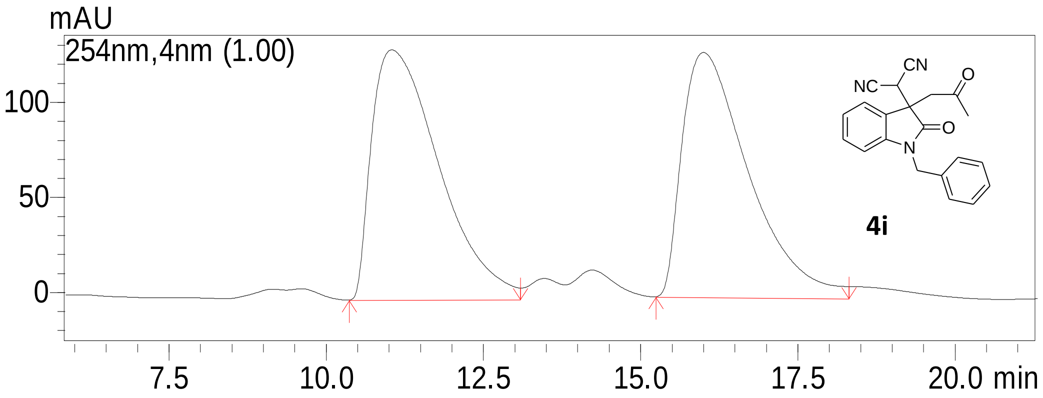

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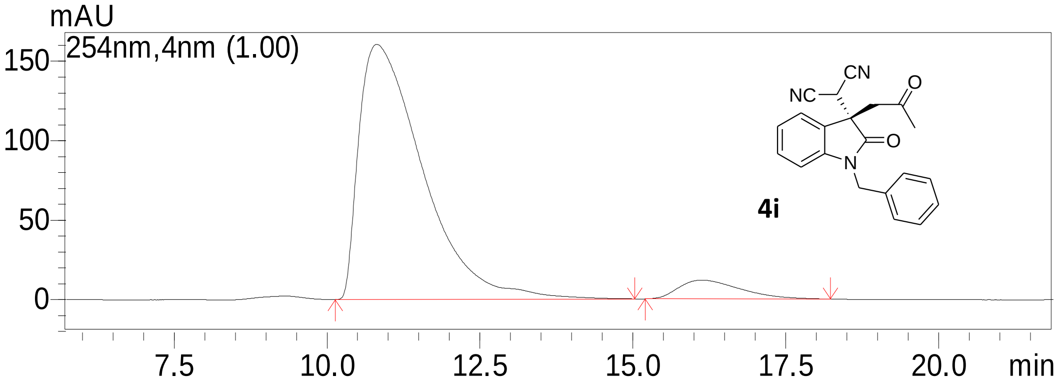

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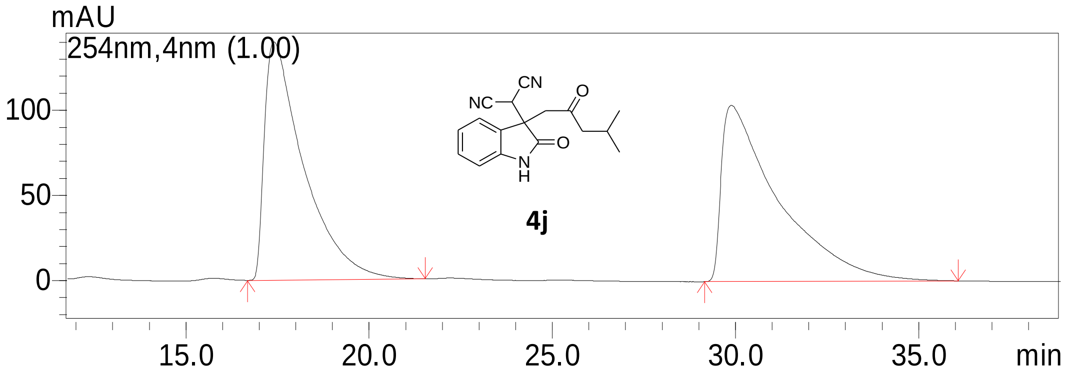

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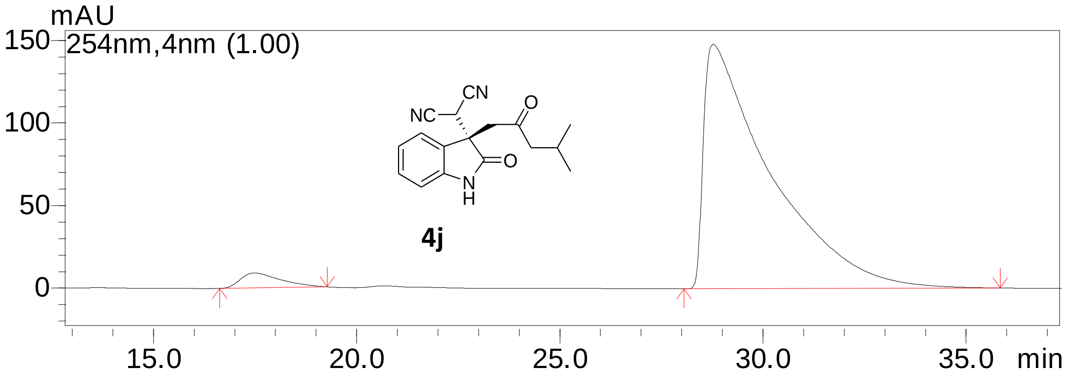

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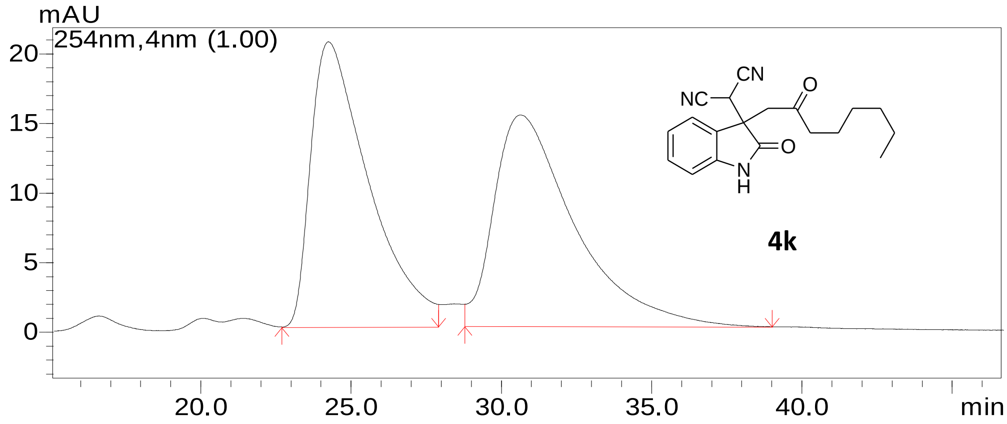

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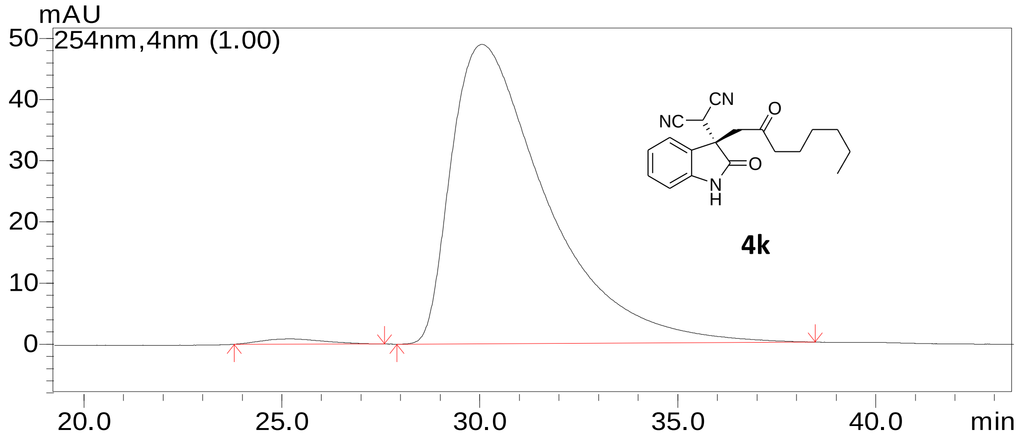

Peak	Ret. Time	Area%
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2	30.052	98.8404